Japanese Kokai Patent Application No. Hei 5[1993]-297496

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PHOTOGRAPHIC ADDITIVE AND SILVER HALIDE PHOTOGRAPHIC MATERIAL

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without using an organic solvent, a swelling agent or a dispersant, as well as a silver halide photographic material in the case of addition into a silver halide emulsion.

Claims

1. A method for the dispersion of a spectral sensitizing dye characterized by the fact that a spectral sensitizing dye that has a solubility at 27°C in an aqueous system essentially free from organic solvent and/or surfactant of 2×10^{-4} to 4×10^{-2} mol/L is added in an amount exceeding the solubility for mechanical dispersion into solid micrograins of less than 1 μm.

2. The method for the dispersion of a spectral sensitizing dye described in Claim 1 characterized by the fact that the solubility at 27°C is 1×10^{-3} to 4×10^{-2} mol/L.

3. A dispersed material of a spectral sensitizing dye characterized by the fact that a spectral sensitizing dye that has a solubility at 27°C in an aqueous system essentially free from organic solvent and/or surfactant of 2×10^{-4} to 4×10^{-2} mol/L is added in an amount exceeding the solubility for mechanical dispersion into solid micrograins of less than 1 μm.

4. The dispersed material of a spectral sensitizing dye described in Claim 3 characterized by the fact that the solubility at 27°C is 1×10^{-3} to 4×10^{-2} mol/L.

5. A silver halide photographic emulsion characterized by the fact that a spectral sensitizing dye prepared by a method in which a spectral sensitizing dye that has a solubility at 27°C in an aqueous system essentially from organic solvent and/or

surfactant of 2×10^{-4} to 4×10^{-2} mol/L is added in an amount exceeding the solubility for mechanical dispersion into solid micrograins of less than 1 μm.

6. The silver halide photographic emulsion described in Claim 5 characterized by the fact that the solubility of the spectral sensitizing dye at 27°C is 1×10^{-3} to 4×10^{-2} mol/L.

7. A silver halide photographic material characterized by the fact that it contains a silver halide photographic emulsion with the addition of a dispersed material of a spectral sensitizing dye prepared by the method in which a spectral sensitizing dye that has a stability at 27°C in an aqueous system essentially free from organic solvent and/or surfactant of 2×10^{-4} to 4×10^{-2} mol/L is added in an amount exceeding the solubility for mechanical dispersion into solid micrograins of less than 1 μm.

8. The silver halide photographic material described in Claim 7 characterized by the fact that the solubility of the spectral sensitizing dye at 27°C is 1×10^{-3} to 4×10^{-2} mol/L.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention relates to a dispersed material of a spectral sensitizing dye with the dispersion of solid micrograins and a silver halide photographic material with the addition of such a sensitizing dye dispersed material.

[0002]

Background of the invention

If a variety of water-insoluble photographic additives are introduced into silver halide emulsions, conventionally, a method is generally and widely carried out in which photographic additives are dissolved in organic solvents like methanol and these solutions are added into silver halide emulsions. However, in such a method, there has been a problem in which an agglomerate is formed in the silver halide emulsion due to the organic solvent, or a problem in which a lumpy or striped coating hindrance occurs during the coating of the silver halide emulsion. Furthermore, operational and environmental problems occur owing to the use of an organic solvent.

[0003]

Instead of such a conventional method, a method has been attempted for the addition, into a silver halide emulsion, of an aqueous dispersed material of an additive obtained by preparation and dispersion as an aqueous solution system in the presence of a swelling agent or a dispersant without using an organic solvent.

[0004]

In other words, in Japanese Kokai Patent Application No. Sho 52[1977]-110012, a method is described, in which a sensitizing agent is pulverized in an aqueous phase in the presence of a dispersant (a surfactant) rendering a constant surface tension, water is removed from the resulting aqueous dispersant that is added as such into a silver halide emulsion after drying, or is added into a silver halide emulsion after dispersion in water or an aqueous gelatin solution.

[0005]

Furthermore, in Japanese Kokai Patent Application No. Sho 53[1978]-102733, a homogeneous mixture (a pasty mixture) consisting of a photographic micrograin additive, sorbitol or other dispersants and gelatin or other protective colloids is prepared. This is noodled, and dried with warm air to form a granular material. The resulting granular material is added into a photographic aqueous colloidal coating composition.

[0006]

Moreover, in U.S. Patent No. 4,006,025, a method is described, in which a spectral sensitizing agent is mixed with water to form a slurry, homogenized or milled in the presence of a surfactant at a temperature of 40-50°C, the spectral sensitizing agent is dispersed uniformly in water, and the dispersed material obtained is added into a silver halide emulsion.

[0007]

However, these addition methods are the methods for the addition of spectral sensitizing agents or other photographic additives in a water system without using organic solvents in any case. In practice, there are the following problems. In other words, since the aqueous dispersant is pulverized by freeze drying or the like, the time required for adsorption onto silver halide grains of spectral sensitizing agents or other additives is long. Therefore, a desired photographic sensitivity cannot be obtained within a short period of time. Furthermore, if such a silver halide emulsion is coated, coating hindrance based on deposits or the like will occur readily. Moreover, since a swelling agent or a dispersant is used in the dispersion of an

additive, the destruction of an emulsified material present in the silver halide emulsion occurs. Adverse effects like an increase in coating hindrance accompanying the high-speed coating of silver halide emulsions occur. Also, the adherence to film of the silver halide photographic material manufactured will be poor. There have been problems in product quality.

[0008]
Objectives of the invention

With respect to the problems described previously, the objective of the present invention is to provide a micrograin-dispersed sensitizing dye having excellent adsorption stability, coating stability, raw storage characteristics and so on with respect to silver halide emulsion grains that can be dispersed rapidly and in a stable manner during the dispersion treatment of a spectral sensitizing dye that is essentially insoluble in water without using an organic solvent, a swelling agent or a dispersant, as well as a silver halide photographic material in the case of addition into a silver halide emulsion.

[0009]
Constitution of the invention

The previously mentioned objective of the present invention is achieved by a method for the dispersion of a spectral sensitizing dye characterized by the fact that a spectral sensitizing dye that has a solubility at 27°C in an aqueous system essentially free from organic solvent and/or surfactant of

1×10^{-4} to 4×10^{-2} mol/L, preferably 2×10^{-4} to 4×10^{-2} mol/L, is added in an amount exceeding the solubility for dispersion into solid micrograins of less than 1 μm mechanically, a dispersed material, a silver halide emulsion with the addition of a dispersed material of said spectral sensitizing dye, and a silver halide photographic material containing said silver halide emulsion.

[0010]

The present invention will be explained specifically in the following.

[0011]

The technology for the mechanical dispersion of organic dyes in aqueous media is known in Japanese Kokai Patent Application No. Hei 3[1991]-2888842. However, this is a method for increasing the diffusion resistance of the organic dye in the photographic material. It is nothing but a simple diffusion-addition method. In contrast to this, the present invention is for the homogeneous and effective adsorption of photographic spectral sensitizing dyes on the surface of silver halide grains. It is different in the objective and effectiveness from the previously mentioned technology of simple diffusion and addition only.

[0012]

In the present invention, organic solvents refer to solvents containing carbon atoms and that are liquids at room temperature. Conventionally, as solvents of sensitizing dyes, in particular, water-miscible organic solvents have been used. For example, alcohols, ketones, nitriles, alkoxy alcohols and so on have been

used. As specific examples, methanol, ethanol, n-propyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, 1,3-propanediol, acetone, acetonitrile, 2-methoxy ethanol, 2-ethoxy ethanol and so on are available.

[0013]

In the present invention, these organic solvents are essentially not contained. Also, as surfactants, anionic surfactants, cationic surfactants, nonionic surfactants and betaine-type surfactants are available.

[0014]

As conventional dispersants of sensitizing dyes, these surfactants have been used. However, in the present invention, these surfactants are essentially not contained.

[0015]

In the present invention, the water system essentially free from organic solvent and/or surfactant is water containing impurities to an extent that does not cause adverse effects on the silver halide photographic emulsion. Even more preferably, it is ion-exchanged water.

[0016]

In the present invention, the solubility of the spectral sensitizing dye with respect to water is 2×10^{-4} to 4×10^{-2} mol/L, even more preferably 1×10^{-3} to 4×10^{-2} mol/L. In other words, if the solubility is lower than this region, the dispersing grain diameter will be very large. Furthermore, since they are not homogeneous, a precipitate of the dispersed material is formed after the completion of dispersion. It is known that a

hindrance occurs in the process of adsorption of a dye on silver halide during the addition of the dispersed material into the silver halide emulsion.

[0017]

Furthermore, if the solubility is higher than this region, the viscosity of the dispersed material will increase beyond what is required. Gas bubbles are engulfed and there is a hindrance in dispersion. Furthermore, at a high solubility, dispersion is impossible. These have been clarified from the research of the present invention.

[0018]

The solubility of the spectral sensitivity dye with respect to water mentioned here has been measured by the method shown in the following.

[0019]

30 mL of ion-exchanged water were added into a 50-mL conical flask. A dye was added into this in an amount without complete dissolution by visual observations. It was maintained at 27°C in a constant-temperature bath. It was stirred with a magnetic stirrer for 10 min. The suspension was filtered with Filter Paper No. 2 manufactured by ToYo Co., Ltd. The filtrate was filtered with a disposable filter by Toso Co., Ltd. The filtrate was diluted appropriately, and the absorbance was measured with a U-3410 spectrophotometer manufactured by Hitachi Co., Ltd. The solubility (mol/L) was determined from this by using the Beer-Lambert law

$$D = \epsilon l c$$

(where D is absorbance, ϵ is a spectral absorption coefficient, l is the length of the cell used in the measurement of absorbance, and c is the concentration (mol/L).

[0020]

Furthermore, the spectral sensitivity dye in the present invention refers to a material that does not cause electron transfer with respect to silver halide during photo excitation in adsorption on silver halide. It does not include an organic dye. In the present invention, any spectral sensitizing dye having a solubility with respect to water in the range of 2×10^{-4} to 4×10^{-2} mol/L is acceptable. Preferably, it is a cyanine dye. Even more preferably, it is a cyanine dye having a hydrophilic group (such as $-SO_3H$, $-COOH$ or the like).

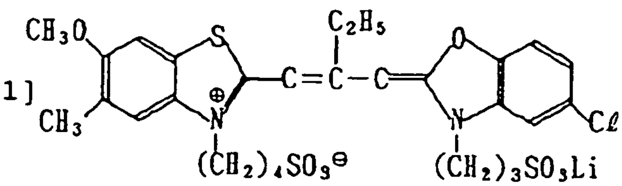
[0021]

Their specific examples and solubilities with respect to water will be given in the following. However, the present invention is not to be restricted to these.

水に対する溶解度
モル/リットル
1

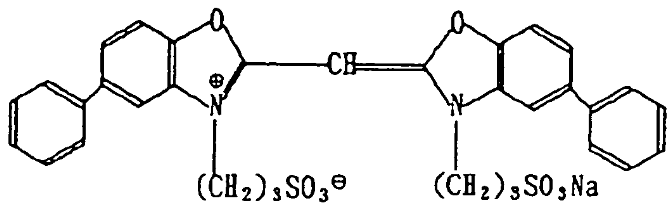
[0022]
[Structure 1]

D－1



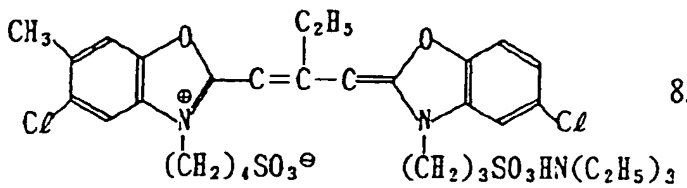
13.1×10^{-3}

D－2



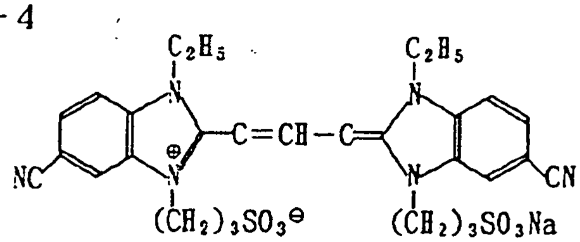
11.0×10^{-3}

D－3



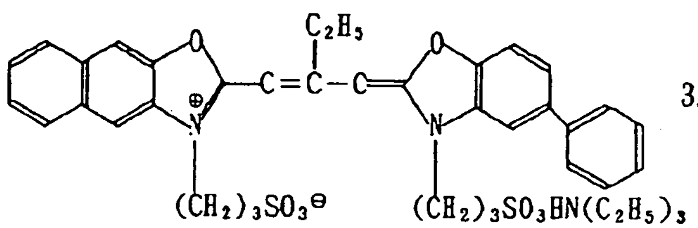
8.21×10^{-3}

D－4



5.75×10^{-3}

D－5



3.69×10^{-3}

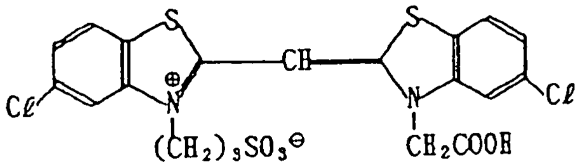
Key: 1 Solubility in water (mol/L)

[0023]

[Structure 2]

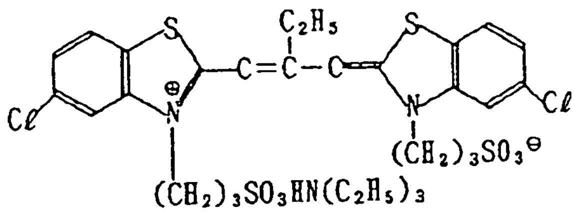
①水に対する溶解度
モル/リットル

D－6



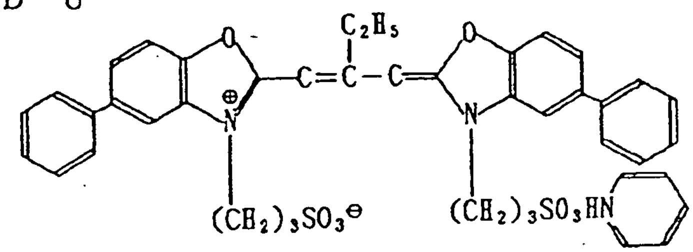
1.63×10⁻³ → 1.63×10^{-3}

D－7



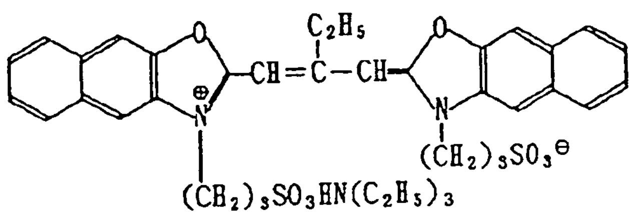
1.42×10^{-3}

D－8



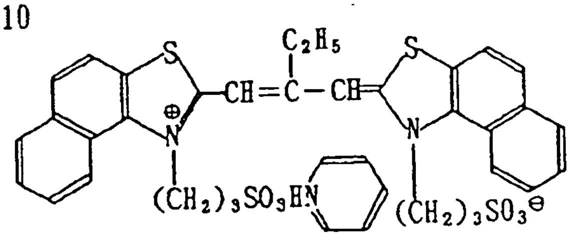
0.89×10^{-3}

D－9



0.37×10^{-3}

D－10



0.30×10^{-3}

Key: 1 Solubility in water (mol/L)

[0024]

In the mechanical pulverization and dispersion of the spectral sensitizing dye in an aqueous solvent in the present invention, a variety of dispersing machines can be used effectively. Specifically, high-speed stirrers, ball mills, sand mills, colloid mills, attrition mills, ultrasonic dispersing machines and so on can be used. In the present invention, high-speed stirrers are preferred.

[0025]

As a high-speed stirring-type dispersing machine, for example, one consisting of a tank (1), a dissolver impeller (2) and a vertical shaft (3), as shown in Figure 1(a), is available. In Figure 1(b), the dissolver (2) is shown.

[0026]

The high-speed stirring-type dispersing machine is a dissolver obtained by the installation of multiple impellers on a vertical shaft or one having multiple-shaft dissolvers with installation of multiple vertical shafts. Furthermore, in addition to the dissolver alone, a high-speed, stirring-type dispersing machine having anchor impellers is an even more preferred one. As a specific operating example, water is introduced into a tank with a variable temperature control, the spectral sensitizing dye powder is then introduced in a constant amount, it is stirrer with a high-speed stirrer on the basis of temperature control for a constant period of time, pulverized and dispersed. There are no special restrictions on pH or temperature during the mechanical dispersion of spectral sensitizing dyes. However, at a low temperature, the desired grain diameters cannot be achieved even if long-term dispersion

is carried out. At a high temperature, re-agglomeration, decomposition or the like occurs. The desired photographic performance cannot be obtained. If the temperature is increased, because of a reduction in the viscosity of the solution, the efficiency of pulverization and dispersion of the solid greatly decrease. Therefore, the dispersion temperature is preferably 15-50°C. Furthermore, in regard to the rotational speed during dispersion, a long period of time is required to obtain the desired grain diameters at a low rotation speed. Moreover, at a high rotation speed, gas bubbles are engulfed and the dispersion efficiency is decreased. Thus, dispersion at 1,000-1,600 rpm is preferred.

[0027]

The fact that the solid micrograins of the spectral sensitizing dye dispersed by the method of the present invention is less than 1 μm means that the grain size according to the diameter of the sphere-equivalent volume is less than 1 μm. It can be measured by an ordinary method.

[0028]

Also, the dispersed material mentioned in the present invention refers to a suspension of a spectral sensitizing dye. Preferable, it is used at 0.2-5.0% as the weight ratio of the spectral sensitizing dye in the suspension.

[0029]

The dispersed material of the spectral sensitizing dye prepared according to the present invention may be added directly into a silver halide emulsion or added after appropriate dilution. Water is used as a diluting liquid at this time.

[0030]

As the silver halide emulsions in the present invention, the materials subjected to physical ripening, chemical ripening and spectral sensitization are used. The additives that can be used in such a process are described in Research Disclosure No. 17,643, No. 18,716 and No. 308,119 (to be abbreviated as RD 17,643, RD 18,716 and RD 308,119, respectively, in the following). The description locations are shown in the following table.

[0031]

Item	Page of RD 308,119
Iodide composition	993 I-Item A
Manufacturing method	993 I-Items A and 994 Item E
Crystal habits (normal crystals)	993 I-Item A
(twinned crystals)	993 I-Item A
Epitaxial	993 I-Item A
Halogen composition (same)	993 I-Item B
(not the same)	993 I-Item B
Halogen conversion	994 I-Item C
Halogen substitution	994 I-Item C
Containing metals	994 I-Item D
Monodisperse	995 I-Item F
Solvent addition	995 I-Item F
Latent image formation position (surface)	995 I-Item G
(inside)	995 I-Item G
Applicable sensitive material negative	995 I-Item H
positive (containing internal fog grains)	995 I-Item H

Used after mixing with an emulsion	995 I-Item J
Desalination	995 II-Item A

In the present invention, silver halide emulsions subjected to physical ripening, chemical ripening and spectral sensitization are used. The additives that are used in such a process are described in Research Disclosure No. 17,643 No. 18,176, and No. 308,119 (to be abbreviated as RD 17,643, RD 18,716 and RD 308,119, respectively, hereafter).

[0032]

The description locations are shown in the following table.

[0033]

Item	Page of RD 308,119	RD 17,643	RD 18,716
Chemical sensitizer	996 III-Items A	23	648
Spectral sensitizer	996 IV-Items A, B, C, D, H, I, J	23-24	648-9
Strong color sensitizer	996 IV-Items A-E, J	23-24	648-9
Antifoggant	998 VI	24-25	649
Stabilizer	998 VI	24-25	649

The publicly known additives that can be used in the present invention are also described in the Research Disclosure mentioned previously.

[0034]

The locations of related description are shown in the following table.

[0035]

Item	Page of RD 308,119	RD 17,643	RD 18,716
Color turbidity inhibitor	1,002 VII-Item I	25	650
Dye picture image stabilizer	1,001 VII-Item J	25	
Whitener	998 V	24	
Ultraviolet absorbent	1,003 VIII-Items C, XIII c	25-26	
Light absorbent	1,003 VIII	25-26	
Light-scattering agent	1,003 VIII		
Filter dye	1,003 VIII	25-26	
Binder	1,003 IX	26	651
Static inhibitor	1,006 XIII	27	650
Film hardener	1,004 X	26	651
Plasticizer	1,006 XII	27	650
Lubricant	1,006 XII	27	650
Activator-coating aid	1,005 XI	26-27	650
Matt agent	1,007 XVI		
Developer (contained in the sensitive material)	1,011 Item XX B		

Furthermore, it is preferable to add, into a photosensitive material, a compound, that reacts with formaldehyde and solidifies, described in U.S. Patent Nos. 4,411,987 and 4,435,503, in order to prevent the deterioration of the photographic performance due to formaldehyde gas.

[0036]

A variety of color couplers can be used in the present invention. Their specific examples are described in the patents described in the previously mentioned Research Disclosure (RD) No. 17,643, VII-C through G.

[0037]

As yellow couplers, those described in, for example, U.S. Patent Nos. 3,933,051, 4,002,620, 4,326,024, 4,401,752, 4,248,961, Japanese Kokoku Patent No. Sho 58[1983]-10739, British Patent Nos. 1,425,020, 1,476,760, U.S. Patent Nos. 3,973,968, 4,314,023, 4,511,649, European Patent No. 279,473A and so on are preferred.

[0038]

As magenta couplers, 5-pyrazolone and pyrazoloazole compounds are preferred. Those described in U.S. Patent Nos. 4,310,619, 4,351,897, European Patent No. 73,636, U.S. Patent Nos. 3,061,432, 3,725,067, U.S. Patent Nos. 3,061,432, 3,725,067, Research Disclosure No. 24,220 (June 1984), Japanese Kokai Patent Application No. Sho 60[1985]-33552, Research Disclosure No. 24,230 (June 1984), Japanese Kokai Patent Application Nos. Sho 60[1985]-43659, Sho 61[1986]-72238, Sho 60[1985]-35730, Sho 55[1980]-118034, Sho 60[1985]-185951, U.S. Patent Nos. 4,500,630, 4,540,654, 4,556,630, International Patent Application No. WO 88/04795 and so on are especially preferred.

[0039]

As cyan couplers, phenol and naphthol couplers can be mentioned. Those described in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,233, 4,269,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, 4,327,173, West

German Patent Application No. 3,329,729, European Patent Nos. 121,365A, 249,453A, U.S. Patent Nos. 3,446,662, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, 4,296,199, Japanese Kokai Patent Application No. Sho 61[1986]-42658 and so on are preferred.

[0040]

As colored couplers for the correction of the undesirable absorption of color-forming dyes, those described in Research Disclosure No. 17,643, VII-Item G, U.S. Patent No. 4,163,670, Japanese Kokoku Patent No. Sho 57[1982]-39413, U.S. Patent Nos. 4,004,929, 4,138,258 and British Patent No. 1,146,368 are preferred. Furthermore, it is preferable to use couplers for the correction of the undesirable absorption of color-forming dyes due to fluorescent dyes released during coupling described in U.S. Patent No. 4,774,181, or couplers having, as detached groups, dye precursor groups, that form dyes by reaction with developers in U.S. Patent No. 4,777,120.

[0041]

As couplers, having appropriate diffusivities of color-forming dyes, those described in U.S. Patent No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570 and West German Patent Application No. 3,234,533 are preferred.

[0042]

Typical examples of polymerized dye-forming couplers are described in U.S. Patent Nos. 3,451,820, 4,080,211, 4,367,282, 4,409,320, 4,576,910, British Patent No. 2,102,173, etc.

[0043]

The couplers that release photographically useful residual groups accompanying coupling can also be used preferably in the

present invention. As DIR couplers that release development inhibitors, those described in the patents described in RD 17,643, VII-Item F mentioned previously, Japanese Kokai Patent Application Nos. Sho 57[1982]-151944, Sho 57[1982]-154234, Sho 60[1985]-184248, Sho 63[1988]-37346, U.S. Patent Nos. 4,248,962, 4,782,012 and so on are preferred.

[0044]

As couplers that release nucleating agents or development accelerators in a picture image form during development, and those described in British Patent Nos. 2,097,140, 2,131,188, Japanese Kokai Patent Application Nos. Sho 59[1984]-157638 and Sho 59[1984]-170840 are preferred.

[0045]

In addition, as couplers that can be used in photosensitive materials of the present invention, competing couplers described in U.S. Patent No. 4,130,427, multiple-equivalent couplers described in U.S. Patent Nos. 4,283,472, 4,338,393 and 4,310,618, DIR-redox-compound-releasing couplers, DIR-coupler-releasing couplers, DIR-coupler releasing redox compounds, or DIR-redox-releasing redox compounds described in Japanese Kokai Patent Application No. Sho 60[1985]-185950, Japanese Kokai Patent Application No. Sho 62[1987]-24252 and so on, couplers releasing dyes that recover color after detachment described in European Patent No. 173,302A, bleaching-accelerator-releasing couplers described in R.D. Nos. 11,449, 24,241, Japanese Kokai Patent Application No. Sho 61[1986]-201247 and so on, couplers releasing ligands described in U.S. Patent No. 4,553,477, couplers releasing leuco dyes described in Japanese Kokai Patent

Application No. Sho 63[1988]-75747, couplers releasing fluorescent dyes described in U.S. Patent No. 4,774,181 and so on can be mentioned.

[0046]

Furthermore, a variety of other couplers can be used in the present invention. Their specific examples are described in the following RD. The related locations are shown in the following.

[0047]

Item	Page of RD 308,119	RD 17,643
Yellow couplers	1,001 VII-Item D	VII Items C through G
Magenta couplers	1,001 VII-Item D	VII Items C through G
Cyan couplers	1,001 VI-Item D	VII Items C through G
Colored couplers	1,002 VII-Item G	VII Item G
DIR couplers	1,001 VII-Item F	VII Item F
BAR couplers	1,002 VII-Item F	
Other useful residual-groups-releasing couplers	1,001 VII-Item F	

The additives that can be used in the present invention can be added by the dispersing method or the like described in RD 308,119 XIV.

[0048]

In the present invention, supports described in previously mentioned RD 17,643, p. 28, RD 18,716,647 [p.]-8 [sic] and RD 308,119 XIX can be used.

[0049]

In the photosensitive material of the present invention, filter layers, intermediate layers and other auxiliary layers described in previously mentioned RD 308,119 XII-Item K may be provided.

[0050]

The photosensitive material of the present invention may have normal layer, reverse layer, unit constitution, and a variety of other layer constitutions described in previously mentioned RD 308,119 VII-Item K.

[0051]

The appropriate supports which can be used in the present invention are described in, for example, previously mentioned RD No. 17,643, p. 28 and RD No. 18,716, from the right column of p. 647 to the left column of p. 648.

[0052]

As specific supports, paper obtained by lamination of polyethylene or the like, polyethylene terephthalate film, baryta paper, cellulose triacetate film and so on can be used. The thickness of the support that can be used is generally 50-200 μm.

[0053]

The present invention is applicable to a variety of color photosensitive materials represented by color negative films for general use or movie use, color reversal films for slide use or television use, color paper, color positive film, and color reversal paper.

[0054]

For the photosensitive material of the present invention, the sum of film thicknesses of all hydrophilic colloidal layers

on the side having emulsion layers is preferably less than 24 μm, even more preferably less than 20 μm, yet even more preferably less than 18 μm. Moreover, the film swelling rate $T_{1/2}$ is preferably less than 30 sec, even more preferably less than 20 sec. The film thickness refers to the film thickness measured at 25°C and relative humidity of 55% (2 days). The film swelling $T_{1/2}$ can be measured according to the publicly known procedure in said technological field. For example, it can be measured using a swellometer of the type described by A. Green et al., Photogr. Sci. Eng., Vol. 19, No. 2, pp. 124-129. $T_{1/2}$ is defined as time to reach a saturated film thickness at 90% of the maximum swelling film thickness reached when it has been treated with a color-forming solution at 30°C for 3 min 15 sec.

[0055]

The film swelling rate $T_{1/2}$ can be adjusted by addition of a film hardener into gelatin as a binder or by variation of temporal conditions after coating. Furthermore, the swelling ratio is preferably 150-400%. The swelling ratio can be calculated from the maximum swelling film thickness under conditions described previously according to the equation: (maximum swelling film thickness - film thickness)/film thickness.

[0056]

The color photographic material according to the present invention can be subjected to development processing by the ordinary methods described in the previously mentioned RD No. 17,643, p. 28-29 and RD No. 18,716, from the left column to the right column of [p.] 615.

[0057]

If the photographic material of the present invention is to be used in a rolled state, it will preferably take a form contained in a cartridge. As the cartridges, the most common one is a cartridge of 135 format at present. In addition, cartridges proposed in the following patents can also be used (Japanese Utility Model No. Sho 58[1983]-67329, Japanese Kokai Patent Application Nos. Sho 58[1983]-181035, Sho 58[1983]-182634, Japanese Utility Model No. Sho 58[1983]-195236, U.S. Patent No. 4,221,479, Japanese Patent Application Nos. Sho 63[1988]-57785, Sho 63[1988]-183344, Sho 63[1988]-325638, Japanese Patent Application Nos. Hei 1[1989]-21862, Hei 1[1989]-25362, Hei 1[1989]-30246, Hei 1[1989]-20222, Hei 1[1989]-21863, Hei 1[1989]-37181, Hei 1[1989]-33108, Hei 1[1989]-85198, Hei 1[1989]-172595, Hei 1[1989]-172594, Hei 1[1989]-172593, U.S. Patent Nos. 4,846,418, 4,848,693 and 4,832,275).

[0058]

Furthermore, the present invention is applicable to "small-scale photographic roll film cartridge and film camera" of Japanese Patent Application No. Hei 4[1992]-16934. To obtain a dye picture image using the photosensitive material of the present invention, the commonly known color development processing can be carried out after exposure.

[0059]

The photosensitive material of the present invention can be subjected to development processing by ordinary methods described in previously mentioned RD 17,643, pp. 28-29, RD 18,716, p. 647, and RD 308,119 XII.

[0060]

Application examples

The effectiveness of the present invention will be verified according to the application examples in the following.

[0061]

Application Example 1

As the high-speed stirring-type dispersing machine that can be used in the present invention, the one shown in Figure 1 was used.

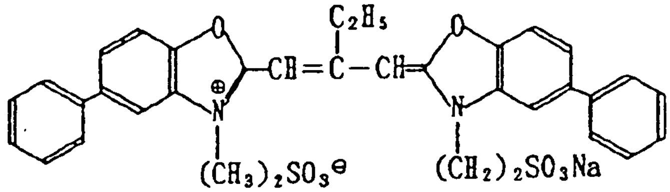
[0062]

For comparison, the following sensitizing dyes were used.

[0063]
[Structure 3]

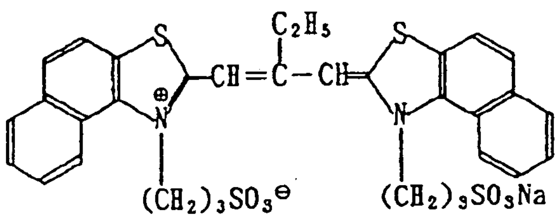
1 水に対する溶解度
モル/リットル

D－11



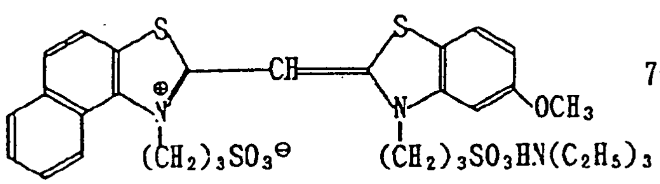
0.18×10⁻³

D－12



0.07×10⁻³

D－13



70.0×10⁻³

Key: 1 Solubility in water (mol/L)

[0064]
(Sample 1)

1.0 g of the spectral sensitizing dye (D-5) mentioned previously was added into 200 g of methanol and dissolved at 27°C to obtain a methanol solution of the spectral sensitizing dye.

[0065]
(Sample 2)

10.0 g of the spectral sensitizing dye (D-5) mentioned previously were added into a mixed solution of 4.9 g of methanol and 485.1 g of water at a temperature preadjusted to 27°C. Next, by stirring with the high-speed stirrer (dissolver) shown in Figure 1 at 3,500 rpm over a period of 30-120 min, a dispersed solution, in which the spectral sensitizing dye was dispersed, was obtained.

[0066]
(Sample 3)

10.0 g of the spectral sensitizing dye (D-5) mentioned previously were added into 490 g of a 0.1% aqueous solution of triisopropyl naphthalene sulfonate at a temperature preadjusted to 27°C. Next, by stirring with the high-speed stirrer (dissolver) shown in Figure 1 at 3,500 rpm over a period of 30-120 min, a dispersed solution, in which the spectral sensitizing dye was dispersed, was obtained.

[0067]
(Sample 4)

10.0 g of the spectral sensitizing dye (D-11) mentioned previously were added into 490 g of water at a temperature preadjusted to 27°C. Next, by stirring with the high-speed stirrer (dissolver) shown in Figure 1 at 3,500 rpm over a period of 30-120 min, a dispersed solution, in which the spectral sensitizing dye was dispersed, was obtained.

[0068]
(Sample 5)

By the same recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-12) mentioned previously was obtained.

[0069]
(Sample 6)

When 10.0 g of the spectral sensitizing dye (D-13) mentioned previously were added into 490 g of water at a temperature preadjusted to 27°C, (D-13) was completely dissolved. It was impossible to disperse (D-13) in water only.

[0070]
(Sample 7)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-9) mentioned previously was obtained.

[0071]
(Sample 8)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-10) mentioned previously was obtained.

[0072]
(Sample 9)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-5) mentioned previously was obtained.

[0073]
(Sample 10)

By the sample recipe as (Sample 1), a methanol solution of the spectral sensitizing dye (D-3) mentioned previously was obtained.

[0074]
(Sample 11)

By the sample recipe as (Sample 1), a methanol solution of the spectral sensitizing dye (D-4) mentioned previously was obtained.

[0075]
(Sample 12)

By the sample recipe as (Sample 1), a methanol solution of the spectral sensitizing dye (D-9) mentioned previously was obtained.

[0076]
(Sample 13)

By the sample recipe as (Sample 1), a methanol solution of the spectral sensitizing dye (D-8) mentioned previously was obtained.

[0077]
(Sample 14)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-3) mentioned previously was obtained.

[0078]
(Sample 15)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-4) mentioned previously was obtained.

[0079]
(Sample 16)

By the sample recipe as (Sample 4), a dispersed solution of the spectral sensitizing dye (D-8) mentioned previously was obtained.

[0080]

The average grain sizes of spectral sensitizing dyes in the dispersed solutions obtained in Samples 2-9 were measured in the state of primary grains immediately after sample preparation. Also, the dispersed states of the dispersed solutions obtained in Samples 2-9 after standing at 27°C for one week were evaluated by visual observation. They are shown in Table I.

[0081]

Table I.

試料 No.	一定時間分散後の平均粒子サイズ(μ) 30分	60分	90分	120分	週間放置後の分散状態	備考
2	0.3	0.2	0.2	0.1	変化なし	比較例
3	0.3	0.2	0.1	0.1	変化なし	比較例
4	2.0	1.8	1.7	1.5	沈降した	比較例
5	3.5	3.0	2.8	2.4	沈降した	比較例
6	—	—	—	—	—	比較例
7	0.5	0.5	0.3	0.3	変化なし	本発明
8	0.6	0.5	0.3	0.3	変化なし	本発明
9	0.4	0.3	0.3	0.2	変化なし	本発明

Key:
1 Sample No.
2 Average grain sizes (μ) after dispersion for a constant time
3 Minutes
4 Dispersed states after standing for one week
5 Remarks
6 No change
7 Comparative example
8 Settled
9 Present invention

[0082]

It is clear from the results of Table I that the samples of the present invention are excellent in dispersion stability.

Application Example 2

(Emulsions 1-4) were prepared according to the following methods.

[0083]
(Emulsion 1)

The methanol solution of the spectral sensitizing dye prepared in Sample 1 was added at 1.0 x 10^{-4} mol per mol of silver halide into a silver halide emulsion subjected to optimum chemical sensitization with sodium thiosulfate and chloroauric acid in Em-4 used in the application example of Japanese Patent Application No. Hei 3[1991]-168850. It was stirred at 55°C for 30 min.

[0084]
(Emulsion 2)

(Sample 2) was used instead of (Sample 1) in (Emulsion 1).

[0085]
(Emulsion 3)

(Sample 3) was used instead of (Sample 1) in (Emulsion 1).

[0086]

(Emulsion 4)

(Sample 9) was used instead of (Sample 1) in (Emulsion 1).

[0087]

Appropriate amounts of these (Emulsions 1-4) were collected. After centrifugal separation, the supernatant liquids were collected. The concentrations of the spectral sensitizing dye (D-5) were measured with a spectrophotometer. The reciprocal of the measured value is a simple measure of adsorption force. With 100 as a reference value, the following results were obtained.

[0088]

	Adsorption force	Remarks
(Emulsion 1)	44	Comparative Example
(Emulsion 2)	86	Comparative Example
(Emulsion 3)	84	Comparative Example
(Emulsion 4)	100	Present invention

It is clear from these results that the emulsion using the sample prepared by the method of the present invention is excellent in adsorption of the sensitizing dye.

[0089]

In the following application example, amounts of addition in the silver halide photographic material show numbers of grams per square meter unless stated otherwise. Furthermore, silver halide and colloidal silver were calculated as silver.

[0090]

Application Example 3

On one side (surface) of a cellulose triacetate film support, underdraw processing was carried out. Next, in between the supports on the opposite side (the back side) of the side subjected to said underdraw processing, layers of the following compositions were formed in sequence from the support side.

[0091]

Back side first layer

Alumina Sol AS-100 (aluminum oxide) (manufactured by Nissan Chemical Ind. Co., Ltd.)	100 mg/m^2
Cellulose diacetate	200 mg/m^2

Back side second layer

Cellulose diacetate	100 mg/m^2
Stearic acid	10 mg/m^2
Silica micrograins (average grain diameter 0.2 μm)	50 mg/m^2

On the surface of the cellulose triacetate film support subjected to underdraw processing, various layers of the following compositions were formed in sequence from the support side to prepare a multilayer color photographic material 101.

[0092]

First layer: Antihalation layer (HC)

Black colloidal silver	0.15 g
UV absorbent (UV-1)	0.20 g
Compound (CC-1)	0.02 g
High-boiling-point solvent (Oil-1)	0.20 g
High-boiling-point solvent (Oil-2)	0.20 g
Gelatin	1.6 g

Second layer: Interlayer (IL-1)

High-boiling-point solvent (Oil-1)	0.5 g
Gelatin	1.3 g

Third layer: Low-sensitivity, red-sensitive emulsion layer (R-L)

Silver iodobromide emulsion (average grain diameter 0.3 μm) (average iodide content 2.0 mol%)	0.4 g
Silver iodobromide agent (average grain diameter 0.4 μm) (average iodide content 8.0 mol%)	0.3 g
Sensitizing dye (S-1) 3.2×10^{-4}	(mol/mol silver)
Sensitizing dye (S-2) 3.1×10^{-4}	(mol/mol silver)
Sensitizing dye (S-3) 0.2×10^{-4}	(mol/mol silver)
Cyan coupler (C-1)	0.50 g
Cyan coupler (C-2)	0.13 g
Colored cyan coupler (CC-1)	0.07 g
DIR compound (D-1)	0.006 g

DIR compound (D-2)	0.01 g
High-boiling-point solvent (Oil-1)	0.55 g
Gelatin	1.0 g

Fourth layer: High-sensitivity, red-sensitive emulsion layer (R-H)

Silver iodobromide emulsion (average grain diameter 0.7 μm) (average iodide content 7.5 mol%)	0.9 g
Sensitizing dye (S-1) 1.7×10^{-4}	(mol/mol silver)
Sensitizing dye (S-2) 1.6×10^{-4}	(mol/mol silver)
Sensitizing dye (S-3) 0.1×10^{-4}	(mol/mol silver)
Cyan coupler (C-2)	0.23 g
Colored cyan coupler (CC-1)	0.03 g
DIR compound (D-2)	0.02 g
High-boiling-point solvent (Oil-1)	0.25 g
Gelatin	1.0 g

Fifth layer: Interlayer (IL-2)

High-boiling-point solvent (Oil-1)	0.5 g
Gelatin	0.8 g

Sixth layer: Low-sensitivity, green-sensitive emulsion layer (G-L)

Silver iodobromide emulsion (average grain diameter 0.4 μm) (average iodide content 8.0 mol%)	0.6 g

Silver iodobromide emulsion (average grain diameter 0.3 μm) (average iodide content 2.0 mol%)	0.2 g
Sensitizing dye (S-4) 6.7×10^{-4}	(mol/mol silver)
Sensitizing dye (S-5) 0.8×10^{-4}	(mol/mol silver)
Magenta coupler (M-1)	0.17
Magenta coupler (M-2)	0.43 g
Colored magenta coupler (CM-1)	0.10 g
DIR compound (D-3)	0.02 g
High-boiling-point solvent (Oil-2)	0.7 g
Gelatin	1.0 g

Seventh layer: High-sensitivity, green-sensitive emulsion layer (G-H)

Silver iodobromide emulsion (average grain diameter 0.7 μm) (average iodide content 7.5 mol%)	0.9 g
Sensitizing dye (S-6) 1.1×10^{-4}	(mol/mol silver)
Sensitizing dye (S-7) 2.0×10^{-4}	(mol/mol silver)
Sensitizing dye (S-8) 0.3×10^{-4}	(mol/mol silver)
Magenta coupler (M-1)	0.30 g
Magenta coupler (M-2)	0.13 g
Colored magenta coupler (CM-1)	0.004 g
DIR compound (D-3)	0.004 g
High-boiling-point solvent (Oil-2)	0.35 g
Gelatin	1.0 g

Eighth layer: Yellow filer layer (YC)

Yellow colloidal silver	0.1 g
Additive (HS-1)	0.07 g
Additive (HS-2)	0.07 g
Additive (SC-1)	0.12 g
High-boiling-point solvent (Oil-2)	0.15 g
Gelatin	1.0 g

Ninth layer: Low-sensitivity, blue-sensitive emulsion layer (B-H)

Silver iodobromide emulsion (average grain diameter 0.3 μm) (average iodide content 2.0 mol%)	0.25 g
Silver iodobromide emulsion (average grain diameter 0.4 μm) (average iodide content 8.0 mol%)	0.25 g
Sensitizing dye (S-9) 5.8×10^{-4}	(mol/mol silver)
Yellow coupler (Y-1)	0.6 g
Yellow coupler (Y-2)	0.32 g
DIR compound (D-1)	0.003 g
DIR compound (D-2)	0.006 g
High-boiling-point solvent (Oil-2)	0.18 g
Gelatin	1.3 g

Tenth layer: High-sensitivity, blue-sensitive emulsion layer (B-H)

Silver iodobromide emulsion (average grain diameter 0.8 μm) (average iodide content 8.5 mol%)	0.5 g
Sensitizing dye (S-10) 2.0×10^{-4}	(mol/mol silver)
Sensitizing dye (S-11) 1.2×10^{-4}	(mol/mol silver)
Yellow coupler (Y-1)	0.18 g
Yellow coupler (Y-2)	0.10 g
High-boiling-point solvent (Oil-2)	0.05 g
Gelatin	1.0 g

Eleventh layer: First protective layer (PRO-1)

Silver iodobromide emulsion (average grain diameter 0.08 μm)	0.3 g
Ultraviolet adsorbent (UV-1)	0.07 g
Ultraviolet adsorbent (UV-2)	0.10 g
Additive (HS-1)	0.2 g
Additive (HS-2)	0.1 g
High-boiling-point solvent (Oil-1)	0.07 g
High-boiling-point solvent (Oil-3)	0.07
Gelatin	0.8 g

Twelfth layer: Second protective layer (PRO-2)

Compound A	0.04 g
Compound B	0.004 g
Polymethyl methacrylate (average grain diameter 0.3 μm)	0.02 g

Methyl methacrylate:ethyl methacrylate:methacrylic acid = 3:3:4 (weight ratio) copolymer (average grain diameter 3 μm) 0.13 g

Gelatin 0.5 g

The silver iodobromide emulsion used in the tenth layer was prepared by the following method.

[0093]

By using monodisperse silver iodobromide grains (silver iodide content 2 mol%) with an average grain diameter of 0.33 μm as seed crystals, a silver iodobromide emulsion was prepared by the double-jet method.

[0094]

Solution <G-1> was maintained at temperature 70°C, pAg 7.8, and pH 7.0. While it was being stirred well, a seed emulsin equivalent to 0.34 mol was added.

[0095]

After <the formation of the internal high-iodide phase-core phase>, while <H-1> and <S-1> were maintained at a flow rate ratio of 1:1, 86 min were required for addition at an accelerated flow rate (the flow rate at the end was 3.6 times of the initial flow rate).

[0096]

In continuation of <the external low-iodide phase-shell phase>, while pAg was maintained at 10.1 and pH at 6.0, <H-2> and <S-2> were added, requiring 65 min, at an accelerated flow rate (the flow rate at the end being 5.2 times the initial flow rate) and a flow rate ratio of 1:1.

[0097]

The pAg and pH during grain formation were controlled using an aqueous potassium bromide solution and an aqueous 56% acetic acid solution. After the formation of grains, a water-washing treatment was carried out by the ordinary flocculation method. Afterwards, gelatin was added and redispersed. At 40°C, pH and pAg were adjusted to 5.8 and 8.06, respectively.

[0098]

The emulsion obtained was a monodisperse emulsion containing octahedral silver iodobromide grains with an average grain diameter of 0.80 μm, a distribution width of 12.4% and a silver iodide content of 8.5 mol%.

[0099]

<G-1>

Ossein gelatin	100.0 g
A 10 wt% method solution of Compound I	25 mL
Aqueous 28% ammonia solution	440.0 mL
Aqueous 56% acetic acid solution	660.0 mL
Water added to	5,000.0 mL

[0100]

[Structure 4]

Compound I

$$HO(CH_2CH_2O)m(\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2O)_{17}(CH_2CH_2O)nH$$

(average molecular weight ≒ 1300)

[0101]

<H-1>

Ossein gelatin	82.4 g
Potassium bromide	151.6 g
Potassium iodide	90.6 g
Finished with water	1030.5 mL

<S-1>

Silver nitrate	309.2 g
Aqueous 28% ammonia solution	Equivalent
Finished with water	1030.5 mL

<H-2>

Ossein gelatin	302.1 g
Potassium bromide	770.0 g
Potassium iodide	33.2 g
Finished with water	3776.8 mL

<S-2>

Silver nitrate	1133.0 g
Aqueous 28% ammonium solution	Equivalent
Finished with water	3776.8 mL

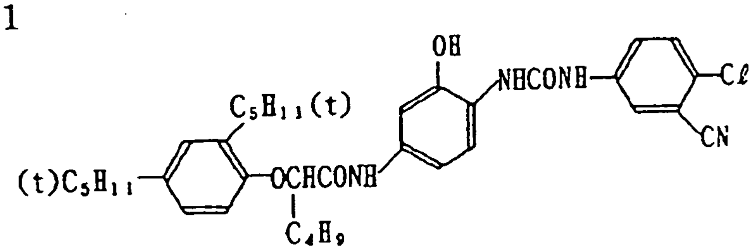
By the same method, the average grain diameter of seed crystals, temperature, pAg, pH, flow rate, addition time and halide composition were varied. The previously mentioned various emulsions with different average grain diameters and silver iodide contents were prepared.

[0102]

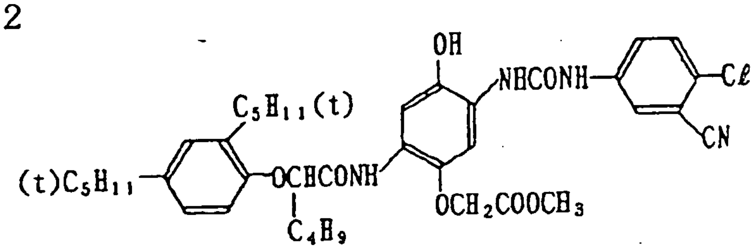
In any case, distribution with 20% was the following core/shell monodisperse emulsions. Each of the emulsions was subjected to an optimum chemical ripening in the presence of sodium thiosulfate, chloroauric acid and ammonium thiocyanate. A sensitizing dye, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and 1-phenyl-5-mercaptotetrazole were added.

[0103]
[Structure 5]

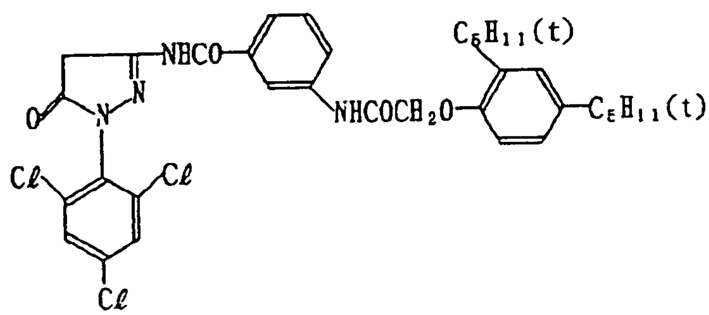
C − 1



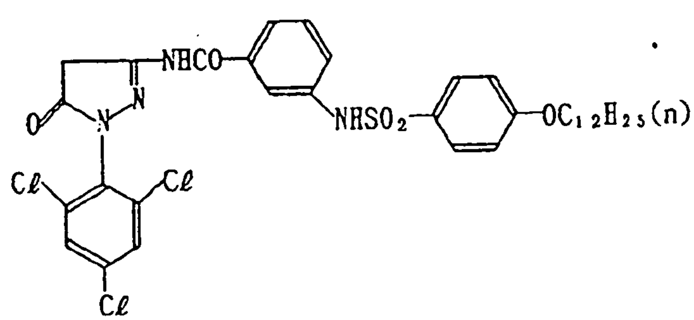
C − 2



M − 1



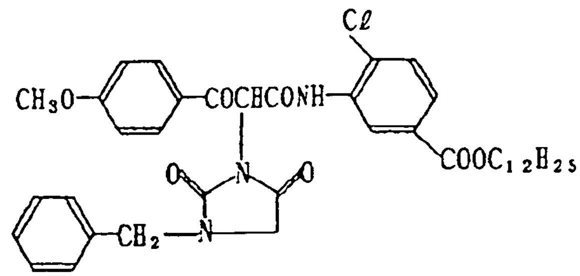
M − 2



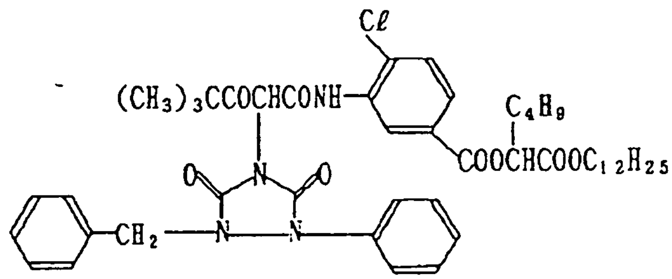
[0104]

[Structure 6]

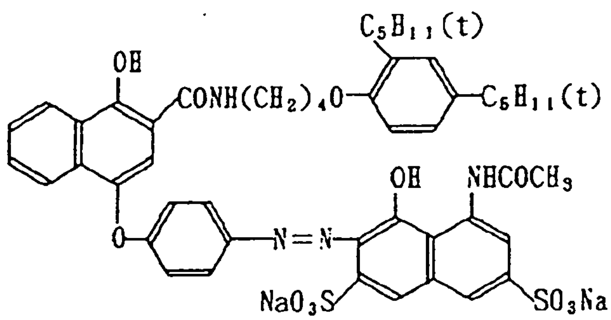
Y－1



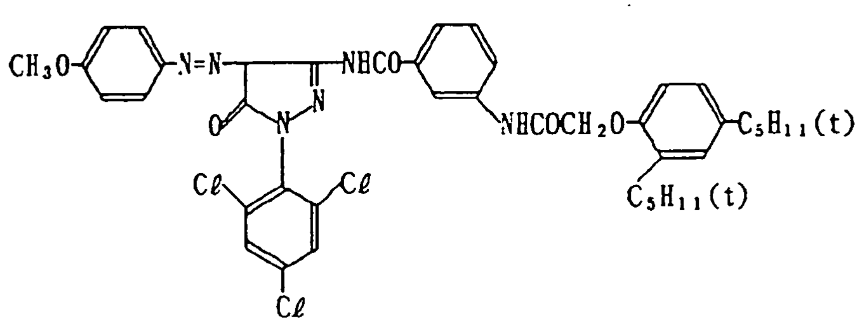
Y－2



CC－1



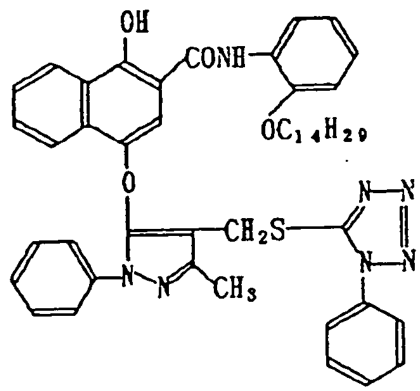
CM－1



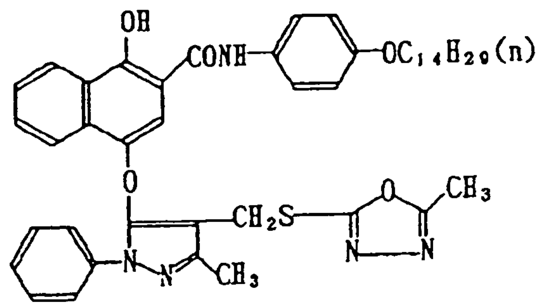
[0105]

[Structure 7]

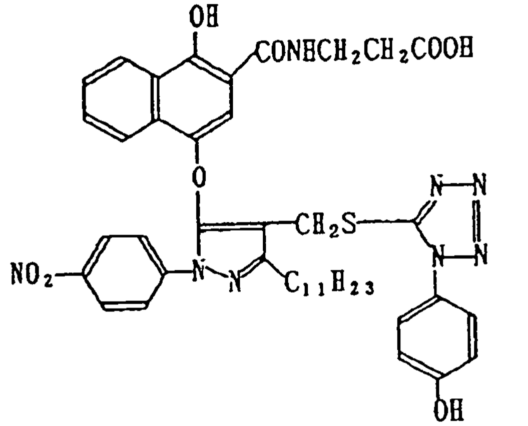
D - 1



D - 2



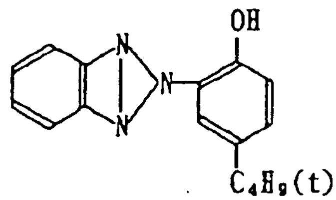
D - 3



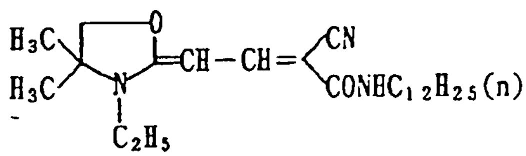
[0106]

[Structure 8]

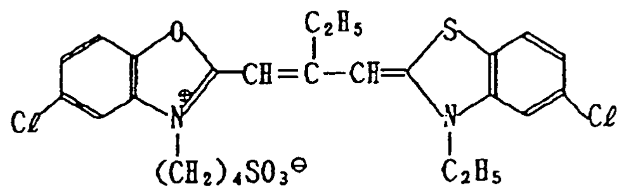
UV－1



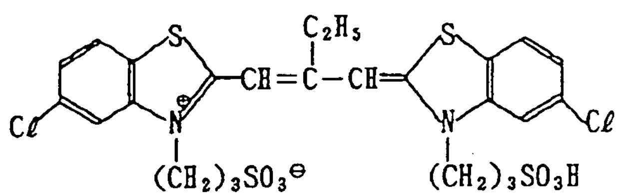
UV－2



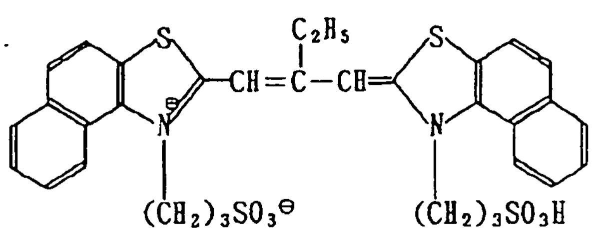
S－1



S－2



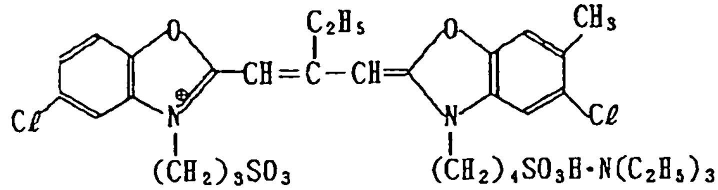
S－3



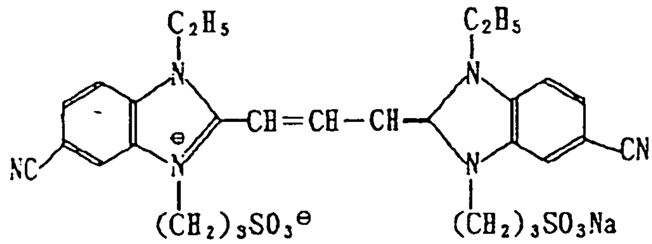
[0107]

[Structure 9]

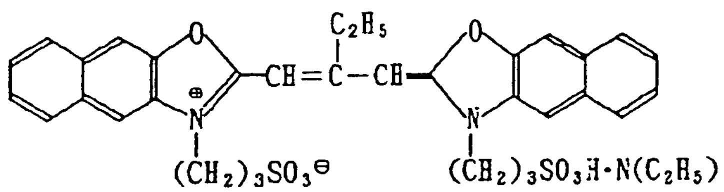
S—4



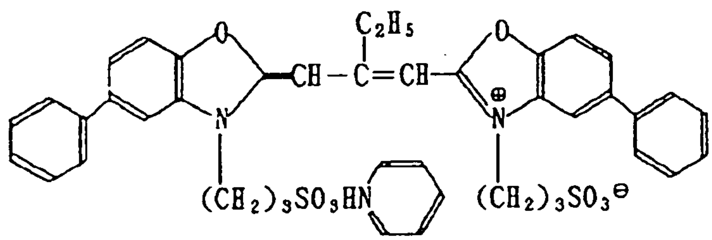
S—5



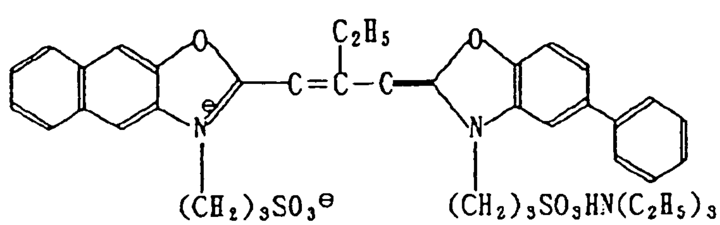
S—6



S—7

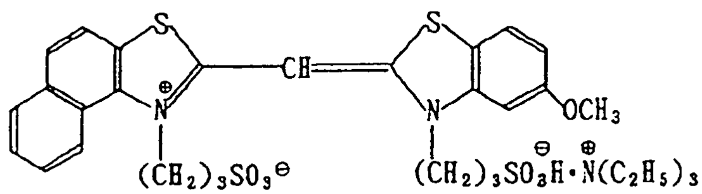


S—8

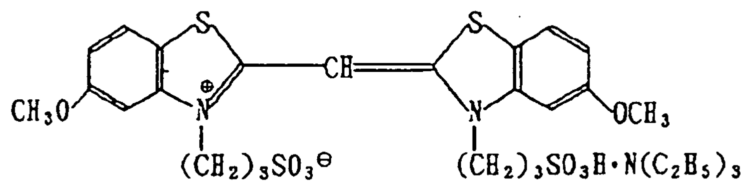


[0108]
[Structure 10]

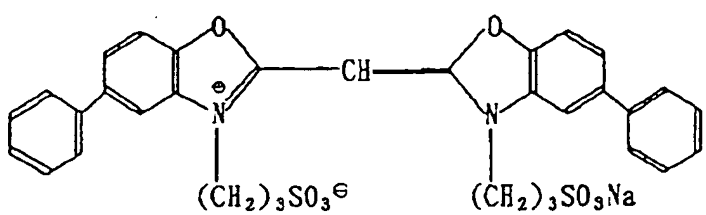
S－9



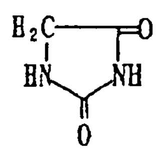
S－10



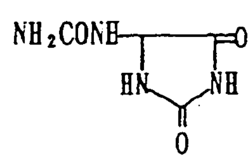
S－11



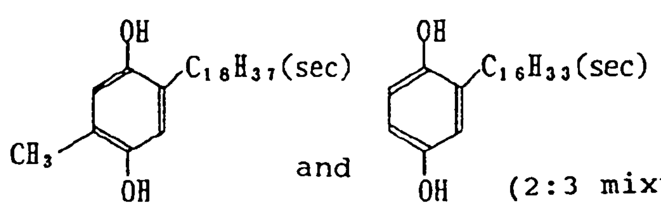
HS－1



HS－2



SC－1

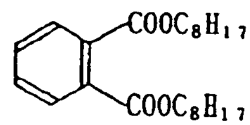


(2:3 mixture)

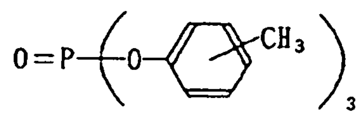
[0109]

[Structure 11]

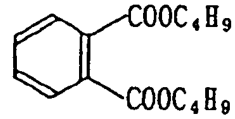
Oil−1



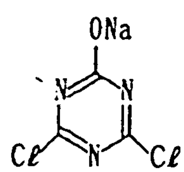
Oil−2



Oil−3

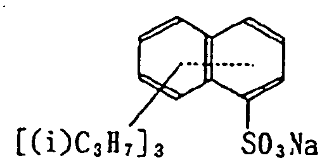


H−1

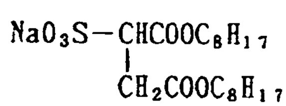


H−2

SU−1

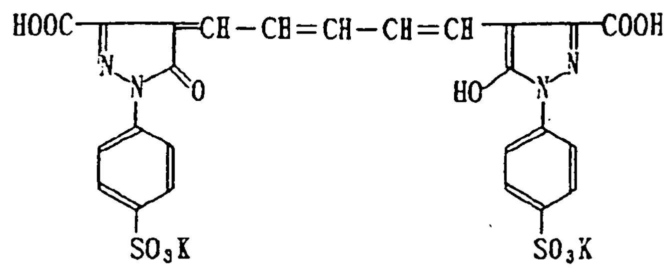


SU−2

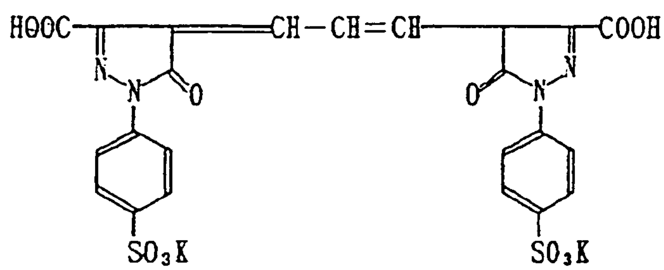


[0110]
[Structure 12]

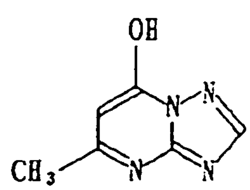
A I − 4



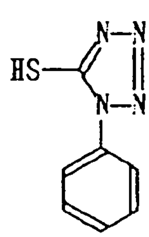
A I − 5



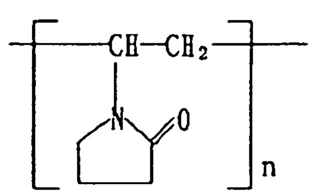
S T − 1



A F − 1



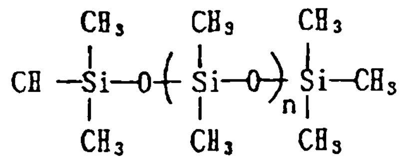
A F − 2



[0111]

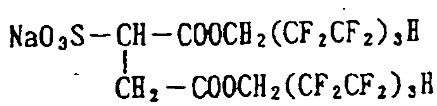
[Structure 13]

Compound A



(average molecular weight = 30,000)

Compound B



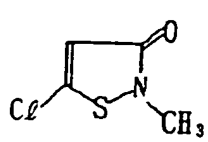
[0112]

The photosensitive material 101 described previously further contains compounds SU-1, SU-2, viscosity-adjusting agent, film-hardening agents H-1, H-2, stabilizer ST-1, antifoggants AF-1, AF-2 (those with weight-average molecular weights of 10,000 and 1,100,000), dyes AI-1, AI-2 and compound DI-1 (9.4 mg/m^2).

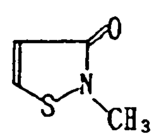
[0113]

[Structure 14]

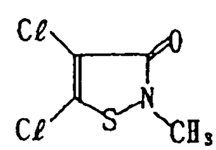
DI-1 (a mixture of the following three components)



(Component A)



(Component B)



(Component C)

A:B:C = 50:46:4 (molar ratios)

[0114]

(Sensitive material A)

In the sixth layer of the color photosensitive material 101 mentioned previously, (Sample 10) was used as (S-4) and (Sample 11) was used as (S-5). Furthermore, in the seventh layer, (Sample 12) was used as S-6), (Sample 13) as (S-7) and (Sample 1) as (S-8).

[0115]

(Sample B)

In the sixth layer of the color photographic material 101 mentioned previously, (Sample 14) was used a (S-4) and (Sample 15) was used as (S-5). Also, in the seventh layer, (Sample 7) was used as (S-6), (Sample 16) as (S-7) and (Sample 9) as (S-8).

[0116]

White light exposure was carried out for (Sensitive material A) and (Sensitive material B) prepared above via a sensitometric step wedge. Treatment was carried out under the following conditions.

4-Amino-3-methyl-N-ethyl-(β-hydroxyethyl)aniline sulfate 4.5 g

Diethylenetriaminepentaacetic acid 3.0 g

Potassium hydroxide 1.2 g

Water was added to 1 L. By using potassium hydroxide or 20% sulfuric acid, pH was adjusted to 10.06.

[0120]

Color-forming development make-up solution

Water	800 mL
Potassium carbonate	35 g
Sodium bicarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1 mg
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate	6.3 g
Potassium hydroxide	2.0 g
Diethylenetriaminepentaacetic acid	3.0 g

Water was added to 1 L. Potassium hydroxide or 0% sulfuric acid was used to adjust pH to 10.18.

[0121]

Bleaching solution

Water	700 mL
1,3-Diaminoproanetetraacetic acid iron(III) ammonium salt	125 g
Ethylenediaminetetraacetic acid	2 g

Sodium nitrate	40 g
Ammonium bromide	150 g
Glacial acetic acid	40 g

Water was added to 1 L. An aqueous ammonia solution or glacial acid was used to adjust pH to 4.4.

[0122]

Bleaching make-up solution

Water	700 mL
1,3-Diaminopropanetetraacetic acid iron(III) ammonium salt	175 g
Ethylenediaminetetraacetic acid	2 g
Sodium nitrate	50 g
Ammonium bromide	200 g
Glacial acetic acid	56 g

An aqueous ammonia solution or glacial acetic acid was used to adjust pH to 4.0, and then water was added to 1 L.

[0123]

Fixing solution

Water	800 mL
Ammonium thiocyanate	120 g
Ammonium thiosulfate	150 g
Sodium sulfite	15 g
Ethylenediaminetetraacetic acid	2 g

An aqueous ammonia solution or glacial acetic acid was used to adjust pH to 6.2, and then water was added to 1 L.

[0124]

<u>Fixing make-up solution</u>

Water	800 mL
Ammonium thiocyanate	150 g
Ammonium thiosulfate	180 g
Sodium sulfite	20 g
Ethylenediaminetetraacetic acid	2 g

An aqueous ammonia solution or glacial acetic acid was used to adjust pH to 6.5, and then water was added to 1 L.

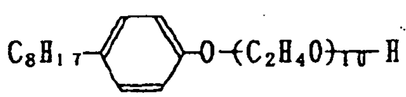
[0125]

<u>Stabilizing solution and stabilization make-up solution</u>

Water	900 mL

[0126]

[Structure 15]



2.0 g

[0127]

Dimethylolurea	0.5 g
Hexamethylenetetramine	0.2 g
1,2-Benzisothiazolin-3-one	0.1 g
Siloxane (L-77, manufactured by UCC)	0.1 g
Aqueous ammonia solution	0.5 mL

Water was added to 1 L, and then an aqueous ammonia solution or 50% sulfuric acid was used to adjust pH to 8.5.

[0128]

The effectiveness of the present invention was also obtained from a photosensitive material prepared in the same manner as the photosensitive material 101 except that the back side first layer and the back side second layer were added into the following composition in the photosensitive material 101.

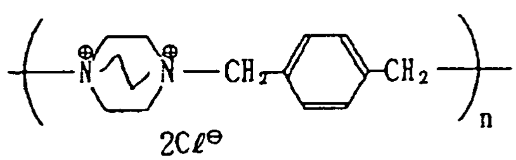
[0129]

Back side first layer

[0130]

[Structure 16]

Ion-type polymer 0.2 g/m^2



(n=30)

[0131]

Back side second layer

Cellulose diacetate	107.6 mg/m^2
Aerosil [transliteration] 200 (grain diameter 0.2 μm silica micrograins) (manufactured by Nippon Aerosil Co., Ltd.)	10.8 mg/^{2}
Citric acid half ethyl ester	6.4 mg/m^2

Next, (photosensitive material A) and (photosensitive material B) prepared were allowed to stand under an atmosphere of 40°C and a relative humidity of 80% for 7 days to carry out the

raw storage characteristics test by forced deterioration. The same exposure as the untested sample was rendered, and the same development processing was carried out.

[0132]

The fog increment (ΔFog) of the sample after forced deterioration with respect to the untested sample and the relative sensitivity (S) of the sample after forced deterioration when the sensitivity of the untested sample was set at 100 were measured.

[0133]

	ΔFog	S	Remarks
Sensitive material A	0.05	85	Comparative Example
Sensitive material B	0.03	95	Present invention

It is clear from these results that the sensitive materials using the samples prepared by the method of the present invention are excellent.

[0134]

Effectiveness of the present invention

By the manufacturing method of the present invention, an aqueous dispersed solution of photographic additives can be manufactured rapidly and effectively. By using this dispersed solution, adsorption onto silver halide grains does not require a long period of time. Within a constant time frame, the desired sensitivity can be obtained. The raw storage characteristics of silver halide color photographic materials are also improved. Furthermore, it is possible to prevent the occurrence of coating malfunctions due to deposits or the like during the coating of

silver halide photographic emulsion. When a photographic additive essentially insoluble in water is added into an aqueous system, it can be carried out even without using swelling agents or dispersants which are considered to be necessary conventionally. Therefore, destruction of the emulsified material, adverse effects of high-speed coating, poor adherence, and other adverse effects can be prevented. Furthermore, the state of adsorption of photographic additives onto silver halide grains can be improved.

<u>Brief explanation of the figures</u>

Figure 1.

(a) A schematic diagram of a high-speed stirring-type dispersing machine

(b) An isometric diagram of an impeller

Explanation of the symbols

1. Tank
2. Dissolver
3. Vertical shaft
4. Solution to be dispersed
5. Impeller

6,7. Shuttlecocks

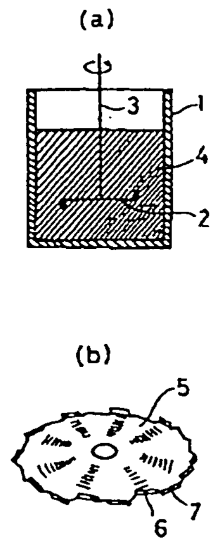


Figure 1